Kinetic information and models used for its extraction

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Abstract

The properties are analyzed of kinetic information obtained in the light of the models commonly used in heterogeneous kinetics. It is shown that the application of models corresponding to different hypothetical mechanisms for describing a process does not permit information to be obtained about its mechanism. The Arrhenius model permits one to obtain only the gross values of the parameters, on the basis of which information on both the real mechanism of the process and its kinetics beyond the experimental temperature range can be obtained

INTRODUCTION

In 1965, in their work [1] devoted to estimating the kinetic constants of chemical reactions, the well known American statisticians Box and Hunter wrote: "Data themselves cannot produce information; they only produce information in the light of a particular model". This idea is remarkable for pointing unequivocally to the active role played by models in extracting kinetic information. Indeed, as we are unable to measure experimentally the kinetic parameters (rate constant, reaction order, pre-exponent, activation energy), we estimate them by means of models whose nature inevitably leaves its imprint on the properties of the kinetic information.

In the present paper, an attempt is made to analyze the properties of kinetic information obtained in the light of the models commonly used in heterogeneous kinetics. To do this, we shall first factually explain the concepts of kinetic information and models. Let us begin with the rate equation of the process

$$dw/dt = k(T)f(w) \tag{1}$$

This model is based on the hypothesis that the contributions of the temperature, $k(T)$, and conversion, $f(w)$, components to the rate of the

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process dw/dt are independent. Information about each of these components is extracted in the light of the corresponding models. The temperature component is described by the known Arrhenius model

$$k(T) = A \exp(-E/RT) \tag{2}$$

at the basis of which lies the assumption of exponential temperature dependence of the process rate. The carriers of the kinetic information obtained in the light of the model given by eqn. (2) are the Arrhenius parameters (AP) — A and E. For describing changes in the process rate caused by a change in the transformation degree w, one uses a wide set of diverse models $f(w)$, at the basis of which lie various theoretical ideas about the mechanism of the process development. The carrier of information about the conversion component is the model itself in its explicit form.

Of course, before analysing the properties of information obtained in the light of the above-mentioned models, we should first raise the question as to their adequacy in the field of heterogeneous kinetics, because the model's adequacy determines the reliability of the information. It should be recognized, however, that this question is purely speculative in nature; to this day, despite unsparing criticism of these models, no worthy alternative to them has been proposed. Therefore we have no other choice than to assume the adequacy of these models.

WHAT INFORMATION IS PRODUCED BY THE $f(w)$ MODEL?

To extract information from data, it is necessary to have, in addition to models, certain rules for their usage. The rules (or, in other words, the method of using models) are determined by the very nature of the models. So, the model given by eqn. (1), assuming independent contributions of the temperature and the conversion component, points to the method of extracting kinetic information which relies on separation of $k(T)$ and $f(w)$. The model of the process $f(w)$ is represented by a set of alternative equations; thus the method of its determination boils down to the selection (discrimination) of a concrete equation which best describes the experimental curves of dw/dt (or w) versus t.

The discrimination methodology of determining $f(w)$ appeared in isothermal kinetics, where separation of the conversion and temperature components is realized by the regime of performing the experiment ($k(T)$ = const. at T = const.). The kinetic curve obtained under these conditions contains only information about the conversion component, which provides potential legitimacy in choosing $f(w)$ by the discrimination method. The nature of the models, however, makes it impossible to create a method of their unambiguous choice [2–4]. Because it is a formal mathematical

description of an ideal process, a model always gives an incomplete description of the real process. For this reason one and the same real process is successfully described by some set of models whose discrimination is meaningless. In non-isothermal kinetics the discrimination is also incorrect, because the thermoanalytical curve contains information about the temperature and conversion components in nonseparated form. As a result, the ambiguity of choosing $f(w)$ in non-isothermal kinetics acquires an especially pronounced character [3,5].

It is obvious that, if we are unable unambiguously to choose a model, we cannot obtain definite information about the process mechanism. Thus, $f(w)$ in isothermal kinetics is really nothing else but the function approximating the conversion component of the process rate. In non-isothermal kinetics, however, $f(w)$ does not carry even this amount of information. Therefore it is hardly worth taking too seriously attempts to interpret $f(w)$ from the viewpoint of the process mechanism, even if such attempts are based on the data of isothermal kinetics.

WHAT INFORMATION IS PRODUCED BY ARRHENIUS PARAMETERS?

It is hard to say what theoretical ideas lie at the basis of the model given by eqn. (2), since Arrhenius derived the corresponding equation [6] by analogy with the van't Hoff equation. It can simply be noted that Arrhenius himself interpreted the quantity E as the critical amount of energy which molecules must acquire in order to be able to undergo reaction [6]. The similarity of equation (2) to the Eyring equation [7] in transition-state theory permits one to attach to AP the meaning of activation energy (E) and vibration frequency of the activated complex (A). But, as we could assert in the example of determining $f(w)$, the possibility of interpreting kinetic information is not determined simply by the theoretical ideas underlying the model. We shall attempt to see exactly what information is given by experimentally calculated AP.

It should be noted that model (2) is represented unambiguously rather than in the form of a set of alternative equations, as applies to $f(w)$. Thus, to describe the temperature component of the process rate there is no need to use the discrimination method. Nevertheless, this method is extensively used for determining AP. Of course, by substituting the model of the process $f(w)$ into eqn. (1), we can isolate the temperature component of the process rate, which is the indispensable condition for estimating AP. It is obvious that in this case the correctness of estimating AP will depend on how well the chosen form of $f(w)$ describes the conversion component of the process rate.

In isothermal kinetics, for which the discrimination method is legitimate in principle, the ambiguity of determining the model of the process does

not introduce a significant error into the accuracy of estimating AP [8]. Quite a different picture is observed in non-isothermal kinetics. The non-isothermal kinetic curve contains information on the temperature and conversion components in nonseparated form. It is therefore adequately described by practically any model $f(w)$ for which the error of choice is compensated by the corresponding error of estimating the $k(T)$ value and, as a result, the values of AP. The quantitative connection between the errors of choosing $f(w)$ and calculating the activation energy was established by us in [9]. Additionally in [10] it was shown that even minimal errors arising in calculating AP by means of discriminating the process models make it impossible to solve applied kinetic problems connected with predicting the behaviour of the substance being investigated outside the experimental range of temperatures. In consequence of that finding, it seems quite obvious that in principle the discrimination cannot be a correct method for extracting kinetic information from the data of non-isothermal kinetics.

To separate correctly the contributions of the temperature and the conversion component, it is necessary to perform a set of non-isothermal experiments for various heating rates. Under the condition that the mechanism of the process remains unchanged when the heating rate is changed, the time at which the same transformation degree (or its corresponding process rate) is attained in various experiments is determined by the temperature component alone, since $f(w) = $ const. at $w = $ const. This makes it possible to estimate the value of E without recourse to the discrimination of the process models. Such a technique of isolating the temperature component is used in the so-called isoconversion methods (IM) of calculating AP considered in our recent review [11]. In this case the correctness of isolating the temperature component determines the reliability of calculating the activation energy. As to the pre-exponent, its value can easily be estimated by the method of [12].

Now that we have determined the correct method of isolating the temperature component, we can speak of the meaning of information obtained in the light of the model given by eqn. (2). First of all, note that the obtainable values of AP are undoubtedly gross ones from the theoretical and the experimental viewpoint. The transition-state theory attaches to E the meaning of true activation energy, i.e. the activation energy of the elementary reaction of transforming an original substance into products. Theoretically, to assign such a meaning to the value of E calculated by model (2), the above mentioned elementary reaction should, as a minimum requirement, be limiting throughout the entire transformation interval, which is not characteristic of heterogeneous processes. Moreover, it is necessary to have the possibility of measuring experimentally the physical quantity, the change in which is determined by the limiting reaction alone. However, the main thermoanalytical methods (DSC, DTA, TG) which

register the extensive properties of the system do not possess the necessary selectivity.

Despite the fact that the AP calculated by IM are gross ones, they permit a lot of useful kinetic information to be obtained. First, this is information about complex processes, among which are included a clear majority of the processes taking place in substance heating. In [13], an approach is proposed which relies on analysing the dependence of the activation energy calculated by IM on the transformation degree; this approach permits one to establish whether the process under study is simple or complex and to propose a kinetic scheme of the process. Using this approach, interpretable kinetic schemes for the thermolysis of polypropylene [14], tetrazole [15] and ıts polymeric derivatives [16] have been proposed.

Second, information is obtained on the behaviour of the substance being investigated outside the experimental temperature range. On the basis of IM we have developed special algorıthms taking into account the potential complexity of any process in constructing a complete set of predictive dependences [17]. These algorithms have formed the basis for the software KinTool developed by us for kinetic processing of thermoanalytical data. Comparison of the potentialities of KinTool with the software of Mettler and Du Pont thermoanalysers shows [18] that the kinetic calculations made with regard to the potential complexity of the process provıde far more reliable information about the behaviour of a substance outside the experi-mental temperature range.

CONCLUSIONS

The results of the analysis performed here show that kinetic information obtained in the light of the above-considered models does not always comply with the researcher's expectations. Thus, in reality, the description of the conversion component of the process rate by a set of alternatıve $f(w)$ models correspondıng to varıous hypothetical mechanısms gives no information about the mechanism of the process. The use of the Arrhenius model for describing the temperature component previously isolated by IM permits calculation of gross values for the AP which can be effectively used in solving applıed kinetic problems. In addition, the transformation degree dependence of the gross activation energy can serve as a source of informa-tion about the real mechanism of the process.

ACKNOWLEDGEMENT

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